

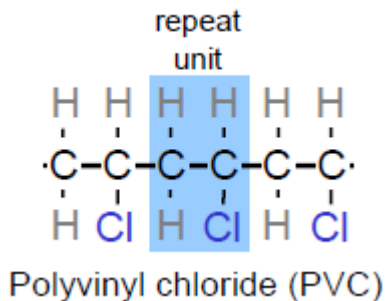
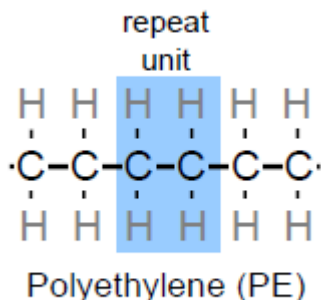
## CD221. LECTURE 7. THE FUNDAMENTAL EQUATION OF A POLYMER MODEL

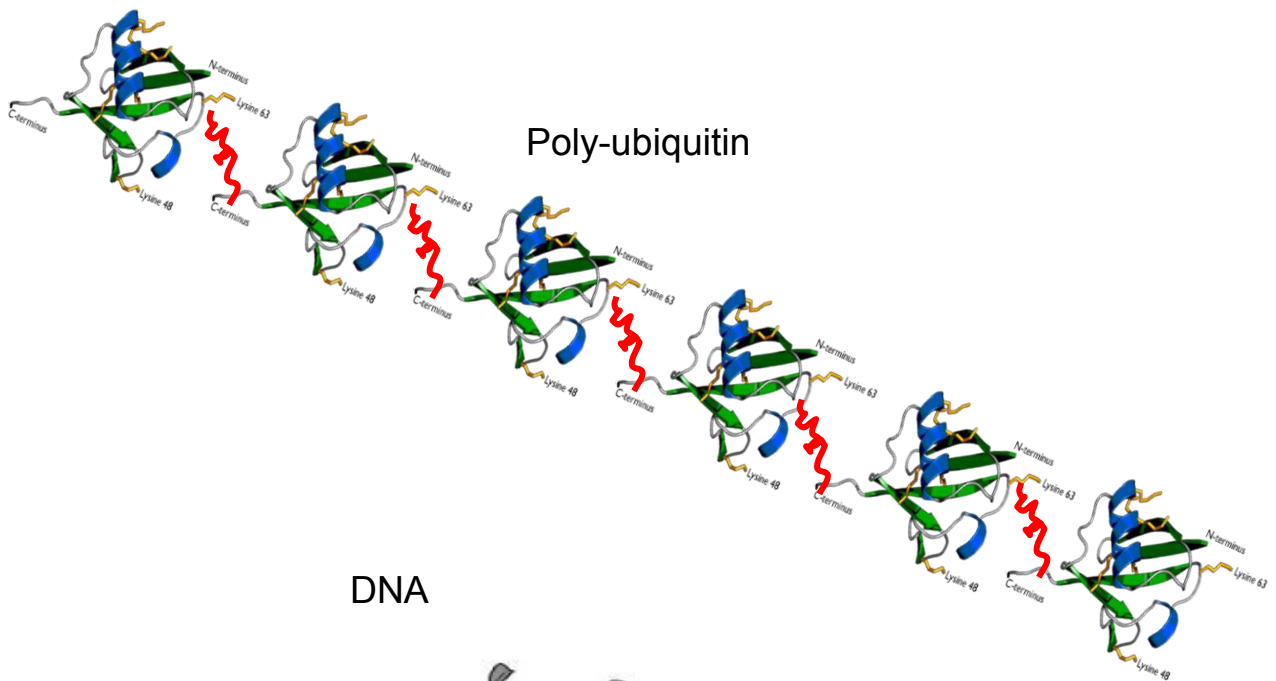
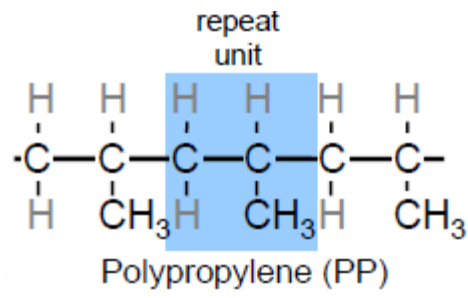
We've now learnt how to obtain an analytical formula for the fundamental equation of an Einstein solid, starting from the expression for its multiplicity. The fundamental equation, in turn, led us to an expression for the temperature dependence of the solid's molar heat capacity, which turned out to be in very reasonable agreement with the known behavior of actual crystalline material. The model did have limitations – it predicted an infinite compressibility, for instance – but the strategy of enumerating the ways in which a fixed amount of energy could be apportioned amongst a system's elementary units was seen to provide a valuable link between microscopic and macroscopic behavior.

We'll now see if the same strategy is successful in understanding the thermodynamics of another class of molecules – polymers.

- Polymers: Some background

Polymers are large molecules made up of many repeated sub-units, all linked together by covalent bonds. Here are a few common examples, along with typical applications:

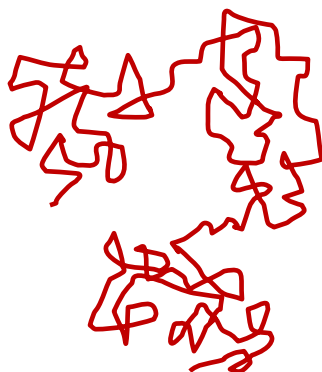




DNA



When dissolved in a suitable solvent, the polymers above are mostly free to flex or twist or rotate around single bonds; in other words, they're able to interconvert relatively easily between a large number of distinct molecular configurations. If you were to represent one of these polymers by just the bonds between one repeat unit and the next, without putting in any of the structural details of the side chains, pendant groups, or other chemical moieties that make different polymers distinctive, one of its typical configurations (projected on to 2-D) might look like this:



A configuration of this kind can be thought of as a microstate of the polymeric system, because, in effect, it specifies which particular bond has which particular orientation with respect to some set of Cartesian axes. There are a huge number of these microstates, and the polymer constantly makes transitions between them (usually on timescales on the order of milliseconds), in much the same way that it can be supposed that a macroscopic object in thermodynamic equilibrium inter-converts between the various microstates available to it. By itself, therefore, a single polymer in solution constitutes the kind of system that is amenable to analysis by statistical mechanical principles.

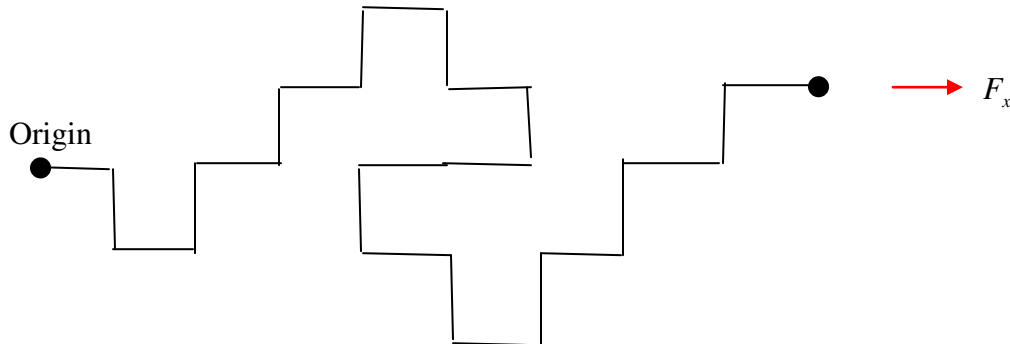
There are many different levels of complexity at which these principles can be applied, ranging from very detailed descriptions that account for all the atoms in the polymer, to very coarse-grained descriptions that represent the polymer as nothing more than a flexible or semi-flexible string.

For the present purposes, we'll develop a model of polymers based on a version of the "bond representation" shown above, and see if the thermodynamic information we extract from it can tell us something about polymer behavior in the bulk. In particular, we'll see if the statistical mechanical formalism of counting microstates can account for an interesting and counter-intuitive phenomenon associated with a rubber band (a polymer), which is that if the rubber band is heated keeping its length (i.e., the average distance from one end of the chain to the other) unchanged, the force pulling the chain inwards – its tension, in other words – increases. (A metallic wire, in contrast, behaves in the opposite way.)

- The Model

We'll think of the polymer as a succession of bonds of fixed length, without worrying about the atoms that connect them. We'll also assume that each of these bonds can only orient itself in one of 4 directions: the positive  $x$ -axis, the negative  $x$ -axis, the positive  $y$ -axis and the negative  $y$ -axis.

So a possible microstate (configuration) of this model polymer might look like this:



Suppose that there are  $N$  of these bonds, each having a length  $b$ . Assume that one end of the polymer is fixed to a point (the black dot) that is taken to be the origin of a 2-D rectangular coordinate system, and that the other end is pulled in the direction of the positive  $x$ -axis by a force (i.e., “tension”)  $F_x$ . ( $F_x$  is the counterpart of the external pressure  $P$  that acts on a gas and maintains it at some volume  $V$ .) To make the model slightly more realistic, we’ll allow for the possibility of having different energies for different configurations. Since we’re trying to say something about the thermodynamics of rubber bands, we’d like the model to penalize configurations that wander too much in the positive or negative  $y$  directions, because a real rubber band is actually made up of a bundle of polymer fibers lying side by side, and this circumstance makes it difficult for individual chains to move too far in the transverse direction.

So let's assume that in either the positive or negative  $x$  orientations a bond does not change the chain's energy, whereas in either the positive or negative  $y$  orientations it changes it by an amount  $+\varepsilon$  (meaning, that in these orientations the energy increases, destabilizing the chain.)

As stated before, a microstate of the chain is a specification of the orientations of individual bonds (each bond having 4 possible orientations.) The macrostate, in this instance, can be taken as a specification of the following parameters: the energy  $U$ , the total number of bonds  $N$ , the number of bonds with positive  $x$  orientation  $N_x^+$ , the number of bonds with negative  $x$  orientation  $N_x^-$ , the number of bonds with positive  $y$  orientation  $N_y^+$ , and the number of bonds with negative  $y$  orientation  $N_y^-$ . (Ordinarily, macrostates would also include some measure of the system's size, such as volume  $V$ ;

we'll see later that we can translate the parameters  $N_x^+$ ,  $N_x^-$ ,  $N_y^+$  and  $N_y^-$  into parameters that define the chain's linear dimensions.) The question now is: how many microstates  $\Omega$  are there for given values of  $U, N, N_x^+, N_x^-, N_y^+$  and  $N_y^-$ ?

We can analyze this problem as follows:

Let's first calculate the number of ways of selecting  $N_x^+$  bonds (having positive  $x$  orientation) out of the total of  $N$  bonds available. From what we've learnt before, that number is

$$\binom{N}{N_x^+} = \frac{N!}{N_x^+! \times (N - N_x^+)!} \quad (1)$$

Having selected these  $N_x^+$  bonds, the number of bonds now remaining is  $N - N_x^+$ . Let's now calculate the number of ways of selecting  $N_x^-$  bonds (having negative  $x$  orientation) out of these  $N - N_x^+$  remaining bonds. That number is

$$\binom{N - N_x^+}{N_x^-} = \frac{(N - N_x^+)!}{N_x^-! \times (N - N_x^+ - N_x^-)!} \quad (2)$$

Having selected these  $N_x^-$  bonds, the number of bonds now remaining is  $N - N_x^+ - N_x^-$ . Let's now calculate the number of ways of selecting  $N_y^+$  bonds (having positive  $y$  orientation) out of these  $N - N_x^+ - N_x^-$  remaining bonds. That number is

$$\binom{N - N_x^+ - N_x^-}{N_y^+} = \frac{(N - N_x^+ - N_x^-)!}{N_y^+! \times (N - N_x^+ - N_x^- - N_y^+)!} \quad (3)$$

Having selected these  $N_y^+$  bonds, the number of bonds now remaining is  $N - N_x^+ - N_x^- - N_y^+$ . Let's now calculate the number of ways of selecting  $N_y^-$  bonds (having negative  $y$  orientation) out of these  $N - N_x^+ - N_x^- - N_y^+$  remaining bonds. That number is

$$\binom{N - N_x^+ - N_x^- - N_y^+}{N_y^-} = \frac{(N - N_x^+ - N_x^- - N_y^+)!}{N_y^-! \times (N - N_x^+ - N_x^- - N_y^+ - N_y^-)!} \quad (4a)$$

$$= \frac{(N - N_x^+ - N_x^- - N_y^+)!}{N_y^-!} \quad (4b)$$

The step leading from Eq. (4a) to (4b) uses the fact that  $N_x^+ + N_x^- + N_y^+ + N_y^- = N$ , and so  $(N - N_x^+ - N_x^- - N_y^+ - N_y^-)! = 0! = 1$ .

All the bonds have now been accounted for. So the total number of ways of dividing up the  $N$  bonds into 4 groups such that  $N_x^+$  are pointing along  $+x$ ,  $N_x^-$  are pointing along  $-x$ ,  $N_y^+$  are pointing along  $+y$  and  $N_y^-$  are pointing along  $-y$  is just the product of the numbers in Eqs. (1), (2), (3) and (4b). That is

$$\Omega = \frac{N!}{N_x^+! \times (N - N_x^+)!} \times \frac{(N - N_x^+)!}{N_x^-! \times (N - N_x^+ - N_x^-)!} \times \frac{(N - N_x^+ - N_x^-)!}{N_y^+! \times (N - N_x^+ - N_x^- - N_y^+)!} \times \frac{(N - N_x^+ - N_x^- - N_y^+)!}{N_y^-!} \quad (5)$$

After cancellation of common terms, Eq. (5) reduces to

$$\Omega = \frac{N!}{N_x^+! \times N_x^-! \times N_y^+! \times N_y^-!} \quad (6)$$

This is very nearly the expression we were after, but as mentioned earlier, it can be re-expressed in terms of parameters of the macrostate that include measures of the polymer's physical dimensions (in addition to  $U$  and  $N$ ). These measures are taken to be  $L_x$ , the net length of the polymer along  $x$ , and  $L_y$ , the net length of the polymer along  $y$ , which are defined as

$$(N_x^+ - N_x^-)b = L_x \quad (7a)$$

$$(N_y^+ - N_y^-)b = L_y \quad (7b)$$

$U$  and  $N$  are also related to  $N_x^+$ ,  $N_x^-$ ,  $N_y^+$  and  $N_y^-$ ; the equations defining them are

$$(N_y^+ + N_y^-)\varepsilon = U \quad (7c)$$

$$(N_x^+ + N_x^- + N_y^+ + N_y^-) = N \quad (7d)$$

Equations (7a) – (7b) can be regarded as 4 equations in the 4 unknowns  $N_x^+$ ,  $N_x^-$ ,  $N_y^+$  and  $N_y^-$ , and they are easily solved to give

$$N_y^+ = \frac{1}{2} \left( \frac{U}{\varepsilon} + \frac{L_y}{b} \right) \equiv \frac{1}{2} (\bar{U} + \bar{L}_y) \quad (8a)$$

$$N_y^- = \frac{1}{2} \left( \frac{U}{\varepsilon} - \frac{L_y}{b} \right) \equiv \frac{1}{2} (\bar{U} - \bar{L}_y) \quad (8b)$$

$$N_x^+ = \frac{1}{2} \left( N - \frac{U}{\varepsilon} + \frac{L_x}{b} \right) \equiv \frac{1}{2} (N - \bar{U} + \bar{L}_x) \quad (8c)$$

$$N_x^- = \frac{1}{2} \left( N - \frac{U}{\varepsilon} - \frac{L_x}{b} \right) \equiv \frac{1}{2} (N - \bar{U} - \bar{L}_x) \quad (8d)$$

where we've introduced the definitions  $\bar{U} = U / \varepsilon$  and  $\bar{L}_\alpha = L_\alpha / b$ ,  $\alpha = x, y$ . Now using Eqs. (8a) – (8b) to eliminate  $N_x^+$ ,  $N_x^-$ ,  $N_y^+$  and  $N_y^-$  from Eq. (6), we find that the multiplicity  $\Omega$  becomes

$$\Omega(\bar{U}, \bar{L}_x, \bar{L}_y, N) = \frac{N!}{\left( \frac{1}{2} (N - \bar{U} + \bar{L}_x) \right)! \times \left( \frac{1}{2} (N - \bar{U} - \bar{L}_x) \right)! \times \left( \frac{1}{2} (\bar{U} + \bar{L}_y) \right)! \times \left( \frac{1}{2} (\bar{U} - \bar{L}_y) \right)!} \quad (9)$$

We're now in a position to calculate the entropy, which we do by substituting Eq. (9) into the Boltzmann equation, applying Stirling's approximation, and simplifying the resulting expression by cancellation of terms. What remains is

$$\begin{aligned} \frac{S}{k_B} = N \ln N - \frac{1}{2} (N - \bar{U} + \bar{L}_x) \ln \left[ \frac{1}{2} (N - \bar{U} + \bar{L}_x) \right] - \frac{1}{2} (N - \bar{U} - \bar{L}_x) \ln \left[ \frac{1}{2} (N - \bar{U} - \bar{L}_x) \right] \\ - \frac{1}{2} (\bar{U} + \bar{L}_y) \ln \left[ \frac{1}{2} (\bar{U} + \bar{L}_y) \right] - \frac{1}{2} (\bar{U} - \bar{L}_y) \ln \left[ \frac{1}{2} (\bar{U} - \bar{L}_y) \right] \end{aligned} \quad (10)$$

This is the fundamental equation of the polymer, and it completes the statistical mechanical part of the calculation. Now we invoke the thermodynamic formalism to determine bulk properties. To begin with, we can calculate the temperature of the system by differentiating (10) with respect to  $U$ . Carrying out this operation, cancelling terms and simplifying, we find that

$$\frac{1}{T} = \frac{1}{\varepsilon} \left( \frac{\partial S}{\partial U} \right)_{N, \bar{L}_x, \bar{L}_y} = \frac{k_B}{2\varepsilon} \ln \left[ \frac{(N - \bar{U} + \bar{L}_x)(N - \bar{U} - \bar{L}_x)}{(\bar{U} + \bar{L}_y)(\bar{U} - \bar{L}_y)} \right]$$

$$= \frac{k_B}{2\varepsilon} \ln \left[ \frac{(N - \bar{U})^2 - \bar{L}_x^2}{\bar{U}^2 - \bar{L}_y^2} \right] \quad (11)$$

Leaving this expression aside for the moment, let's turn to other thermodynamic properties that can be calculated from the fundamental equation. Now in general we know that given  $S = S(U, V, N)$ , we can determine the pressure as  $P/T = (\partial S / \partial V)_{U, N}$ . In the polymer problem,  $\bar{L}_x$  and  $\bar{L}_y$  play the role of  $V$ , while  $-F_x$  (the  $x$  component of the tension) and  $-F_y$  (the  $y$  component of the tension) play the role of  $P$ . Specifically,

$$-\frac{F_x}{T} = \frac{1}{b} \left( \frac{\partial S}{\partial \bar{L}_x} \right)_{\bar{U}, \bar{L}_y, N} \quad (12a)$$

$$-\frac{F_y}{T} = \frac{1}{b} \left( \frac{\partial S}{\partial \bar{L}_y} \right)_{\bar{U}, \bar{L}_x, N} \quad (12b)$$

The reason for the minus signs is the following: in general, when a system like rubber is stretched by some amount  $dL$  by some force  $F$ , work is done on the system, and its energy changes by  $FdL$ . In a thermodynamic setting, then, if  $N$  is a constant,  $dU = TdS + FdL$ . So at constant  $U$ , we have  $-TdS = FdL$ , and hence  $F/T = -(\partial S / \partial L)_{U, N}$ . If the expression for  $S$  in Eq. (10) is separately differentiated with respect to  $\bar{L}_x$  and  $\bar{L}_y$ , and the results simplified by cancellation and reorganization of terms, we find, after using the definitions of Eqs. (12a) and (12b), that

$$-\frac{F_x}{T} = \frac{k_B}{2b} \ln \left( \frac{N - \bar{U} - \bar{L}_x}{N - \bar{U} + \bar{L}_x} \right) \quad (13a)$$

$$-\frac{F_y}{T} = \frac{k_B}{2b} \ln \left( \frac{\bar{U} - \bar{L}_y}{\bar{U} + \bar{L}_y} \right) \quad (13b)$$

Since the polymer actually experiences no tension in the  $y$  direction (see the drawing),  $F_y = 0$ . If we set  $F_y$  to 0 in Eq. (13b), it must follow that  $\bar{U} - \bar{L}_y = \bar{U} + \bar{L}_y$ , which in turn implies that  $\bar{L}_y = 0$  (i.e., there are as many bonds with positive  $y$  orientation as there are with negative  $y$  orientation.) If, further, we now set  $\bar{L}_y = 0$  in Eq. (11) and rearrange the result, we get

$$e^{2\varepsilon / k_B T} = \frac{(N - \bar{U})^2 - \bar{L}_x^2}{\bar{U}^2} \quad (14)$$



At the same time, from Eq. (13a), we have

$$e^{-2F_x b / k_B T} = \frac{N - \bar{U} - \bar{L}_x}{N - \bar{U} + \bar{L}_x} \quad (15)$$

If we eliminate  $\bar{U}$  between Eqs. (14) and (15), we'll get an equation between  $F_x$ ,  $T$  and  $N$  (a “mechanical equation of state”) that will allow us to say something about how temperature affects the dependence of the tension on chain length.

To eliminate  $\bar{U}$ , multiply and divide Eq. (15) by  $N - \bar{U} + \bar{L}_x$ , which leads to

$$e^{-2F_x b / k_B T} = \frac{(N - \bar{U})^2 - \bar{L}_x^2}{(N - \bar{U} + \bar{L}_x)^2} \quad (16)$$

Now divide Eq. (14) by Eq. (16):

$$\begin{aligned} e^{2(\varepsilon + F_x b) / k_B T} &= \left( \frac{N - \bar{U} + \bar{L}_x}{\bar{U}} \right)^2 \\ \therefore \frac{N - \bar{U} + \bar{L}_x}{\bar{U}} &= e^{(\varepsilon + F_x b) / k_B T} \\ \therefore \bar{U} &= \frac{N + \bar{L}_x}{1 + e^{(\varepsilon + F_x b) / k_B T}} \end{aligned} \quad (17)$$

From Eq. (17), we can derive an expression for  $N - \bar{U}$  (which we can then subsequently put back in Eq. (15) and thereby eliminate  $\bar{U}$ ):

$$N - \bar{U} = \frac{N e^{(\varepsilon + F_x b) / k_B T} - \bar{L}_x}{1 + e^{(\varepsilon + F_x b) / k_B T}} \quad (18)$$

Now substituting Eq. (18) into Eq. (15) and simplifying, we find that

$$e^{-2F_x b / k_B T} = \frac{e^{(\varepsilon + F_x b) / k_B T} (N - \bar{L}_x) - 2\bar{L}_x}{e^{(\varepsilon + F_x b) / k_B T} (N + \bar{L}_x)} \quad (19)$$

Therefore,

$$e^{(\varepsilon - F_x b) / k_B T} (N + \bar{L}_x) - e^{(\varepsilon + F_x b) / k_B T} (N - \bar{L}_x) + 2\bar{L}_x = 0 \quad (20)$$

Reorganizing terms and introducing the definitions  $\cosh z = (e^z + e^{-z})/2$  and  $\sinh z = (e^z - e^{-z})/2$ , Eq. (20) can be written as

$$2\bar{L}_x e^{\varepsilon/k_B T} \cosh(F_x b/k_B T) - 2N e^{\varepsilon/k_B T} \sinh(F_x b/k_B T) + 2\bar{L}_x = 0 \quad (21)$$

which can be rewritten as

$$\frac{\bar{L}_x}{N} = \frac{e^{\varepsilon/k_B T} \sinh(F_x b/k_B T)}{1 + e^{\varepsilon/k_B T} \cosh(F_x b/k_B T)} \quad (22)$$

This is the final form of the mechanical equation of state we were looking for.

If the tension in the polymer is not too large (i.e., if  $F_x b/k_B T$  is small), the hyperbolic functions in Eq. (22) can be expanded to leading order, using the following:

$$\begin{aligned} \sinh x &= \frac{1}{2}(e^x - e^{-x}) \approx \frac{1}{2} \left[ 1 + x + \frac{x^2}{2} + \dots - \left( 1 - x - \frac{x^2}{2} + \dots \right) \right] \\ &\approx x + \dots \end{aligned} \quad (23a)$$

$$\begin{aligned} \cosh x &= \frac{1}{2}(e^x + e^{-x}) \approx \frac{1}{2} \left[ 1 + x + \frac{x^2}{2} + \dots + \left( 1 - x - \frac{x^2}{2} + \dots \right) \right] \\ &\approx 1 + \dots \end{aligned} \quad (23b)$$

With the above approximations, Eq. (22) becomes

$$\frac{\bar{L}_x}{N} = \frac{F_x b}{k_B T} \frac{e^{\varepsilon/k_B T}}{1 + e^{\varepsilon/k_B T}} \quad (24)$$

Equivalently, after putting back the definition of  $\bar{L}_x = L_x/b$ , we get

$$L_x = \frac{F_x N b^2}{k_B T} \frac{1}{1 + e^{-\varepsilon/k_B T}} + \dots \quad (25)$$

Now a measure of how easily a substance resists the application of an external pressure is a quantity called the isothermal compressibility, defined as  $\kappa_T = -(1/V)(\partial V/\partial P)_{T,N}$ . A similar measure of how easily polymers are stretched or compressed is a quantity

called the modulus of elasticity  $\kappa_L$ , defined as  $\kappa_L = (1/N)(\partial L_x / \partial F_x)_{T,N}$ . From Eq. (25), this quantity is seen to be

$$\kappa_L = \frac{b^2}{k_B T} \frac{1}{1 + e^{-\varepsilon/k_B T}} + \dots \quad (26)$$

Inspection of Eq. (26) clearly shows that as  $T$  is increased,  $\kappa_L$  decreases, which means that at higher temperatures, a *greater* stretching force is needed to achieve the same change in the polymer's length as occurs at a lower temperature. In other words, at higher temperatures, the chains become *stiffer*. Metal wires behave differently – at higher temperatures, a smaller force is enough to achieve the same extension as occurs at a lower temperature. This prediction of Eq. (26) is in fact in agreement with what is known experimentally – another success of the statistical mechanical formalism.